

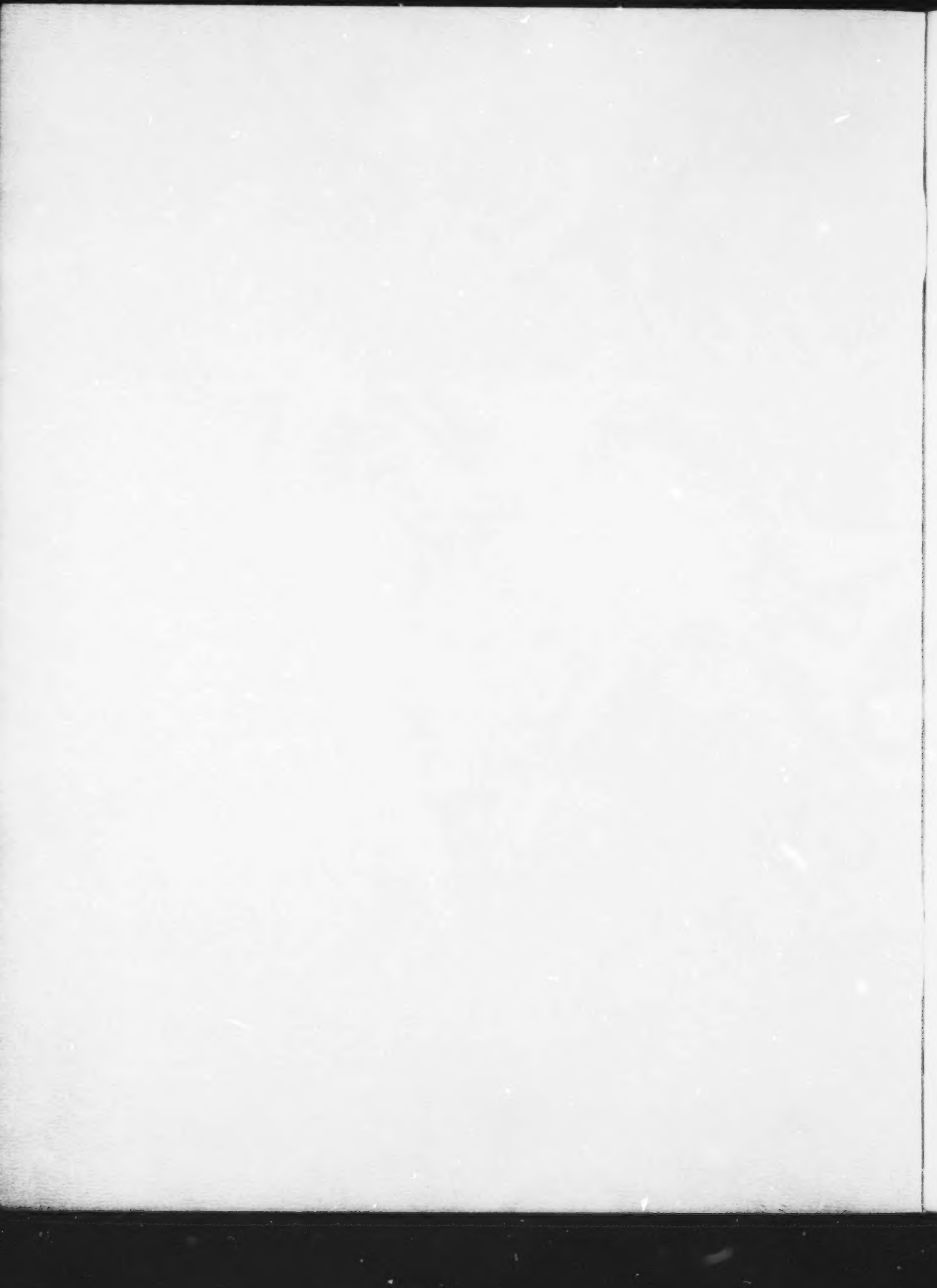


Canadian Centre for
Occupational Health
and Safety

Centre canadien
d'hygiène et de
sécurité au travail

HOW TO WORK SAFELY WITH ORGANIC PEROXIDES

P89 - 9E



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April 1989



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HOW TO WORK SAFELY WITH ORGANIC PEROXIDES

This publication was prepared as a source of general information for health and safety committees and others with an interest in understanding and reducing the occupational hazards of organic peroxides.

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Cette publication est offerte en français sous le titre: Comment travailler en toute sécurité avec les peroxydes organiques.

CCOHS NUMBER P89-9E

ISBN 0-660-13230-3

DSS CATALOGUE NUMBER CC273-2/89-9E

Published 1989

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1. INTRODUCTION

Organic peroxides are present in many workplaces. Everyone who works with these materials must be aware of their hazards and should know how to work safely with them.

This publication provides general information on how to work safely with organic peroxides. Much of this advice can help people work more safely with other hazardous materials too. It is intended for workplaces where organic peroxides are present in storage containers holding 250 litres (55 gallons) or less. It does not cover bulk storage tanks, piping systems, specific processes using organic peroxides or peroxides formed during the storage of chemicals such as ethers.

In most jurisdictions there are legal requirements, such as occupational health and safety regulations and fire and building codes, that apply to the storage, handling and use of organic peroxides. For details contact occupational health and safety officials in the jurisdiction where you work and your local fire and building departments.

Read the container label and material safety data sheet (MSDS) before starting to work with a hazardous material. In most cases, Workplace Hazardous Materials Information System (WHMIS) regulations require the material's supplier or manufacturer to supply a current MSDS if the material is imported or sold for use in a workplace. Many suppliers also provide MSDSs for their products to the Canadian Centre for Occupational Health and Safety (CCOHS). CCOHS makes these MSDSs readily available through its computerized online and compact disc information systems (CCINFOnline and CCINFODisc).

2. WHAT ARE ORGANIC PEROXIDES?

An organic peroxide is any organic (carbon-containing) compound having two oxygen atoms joined together (-O-O-). This chemical group is called a "peroxy" group. Organic peroxides can be severe fire and explosion hazards.

The plastics and rubber industries are the heaviest users of organic peroxides. The terms accelerators, activators, catalysts, cross-linking agents, curing agents, hardeners, initiators and promoters are often used to describe organic peroxides or mixtures which contain organic peroxides. These terms are misleading since they can also refer to materials which are not organic peroxides. A serious accident could result if these substances were mixed with organic peroxides.



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Organic peroxides are available as solids (usually fine powders), liquids or pastes. Some materials, such as water, odourless mineral spirits and several phthalate compounds, do not react with organic peroxides and are often used to dilute them. The diluted mixtures or formulations are less likely to explode when exposed to heat or physical shock than the undiluted organic peroxide. Dilution makes the more chemically unstable peroxides safer to produce, handle, and use. In this publication, the term "organic peroxide" refers to both undiluted and diluted organic peroxides, unless otherwise specified.

Check the supplier labels on chemical product containers. WHMIS classifies organic peroxides as oxidizing materials. WHMIS also classifies many other materials that are not organic peroxides as oxidizing materials. Normally, labels on containers of oxidizing materials will have the hazard symbol shown in Figure 1 on them. Other hazard symbols may also be present, depending on the particular material.

It is wise to treat any unknown material as very hazardous until it is positively identified.



Figure 1 - WHMIS Hazard Symbol for Oxidizing Materials

3. HOW ARE ORGANIC PEROXIDES HAZARDOUS?

Fire and Explosion Hazards

It is the double oxygen of the "peroxy" group that makes organic peroxides both useful and hazardous. The peroxy group is chemically unstable. It can easily decompose, giving off heat at a rate which increases as the temperature rises. Many organic peroxides give off flammable vapours when they decompose. These vapours can easily catch fire.

Most undiluted organic peroxides can catch fire easily and burn very rapidly and intensely. This is because they combine both fuel (carbon) and oxygen in the same compound.

Some organic peroxides are dangerously reactive. They can decompose very rapidly or explosively if they are exposed to only slight heat, friction, mechanical shock or contamination with incompatible materials.

Organic peroxides can also be strong oxidizing agents. Combustible materials contaminated with most organic peroxides can catch fire very easily and burn very intensely.

Hazard Classification

The U.S. National Fire Protection Association (NFPA) has developed a hazard classification system for typical organic peroxide formulations. The NFPA classification system describes the fire and explosion hazards of these formulations in their normal shipping and storage containers. If a formulation is transferred to a different container, the given hazard classification may no longer apply. See NFPA 43B, "Code for the Storage of Organic Peroxide Formulations," for details. In general:

- Class I formulations are a serious explosion hazard. Class I organic peroxides can undergo easily initiated, rapid, and explosive decomposition. Class I includes formulations that are relatively safe only under closely controlled temperatures such as refrigerated storage, or when diluted.
- Class II formulations are severe fire hazards and intermediate explosion hazards. The explosive decomposition is not as rapid, violent or complete as those of Class I formulations. Class II includes some formulations that are relatively safe under controlled temperatures including refrigeration, or when diluted.
- Class III formulations are severe fire hazards and moderate explosion hazards. They burn rapidly and give off intense heat. Many Class III formulations are diluted or require refrigerated storage.
- Class IV formulations are moderate fire hazards that are easily controlled. Many are diluted and some require refrigerated storage.
- Class V formulations are a low or negligible fire hazard. Their combustible packaging materials may pose more of a hazard.

The Appendix lists some typical organic peroxide formulations classified according to their fire and explosion hazard. Some, such as benzoyl peroxide, are found in several NFPA classes, depending on how they are formulated.

The MSDS should describe the conditions that cause an organic peroxide formulation to undergo dangerous chemical reactions.



Other Hazards

Organic peroxides may be toxic or corrosive. Depending on the material, route of exposure (inhalation, eye or skin contact, or swallowing) and dose, they could harm the body.

Corrosive organic peroxides can also attack and destroy metals.

The MSDSs and the container labels should explain all of the hazards of the organic peroxides that you work with.

4. HOW CAN YOU WORK SAFELY WITH ORGANIC PEROXIDES?

Substitution

Substitution can be the best way to avoid or reduce a hazard. But it is not always easy or even possible to find a substitute for a particular organic peroxide used for a certain job. Speak to chemical suppliers to find out if safer substitutes are available. Obtain MSDSs for all possible substitutes. Find out about all hazards (health, fire, corrosivity, chemical reactivity) of these materials before making any changes.

Choose the least hazardous materials that can do the job effectively and safely. Learn how to work safely with them too.

Ventilation

Well-designed and -maintained ventilation systems remove airborne organic peroxides from the workplace and reduce their hazards.

The amount and type of ventilation needed depends on such things as the type of job, the kind and amount of materials used, and the size and layout of the work area.

An assessment of the particular ways a workplace stores, handles, uses and disposes of its organic peroxides is the best way to find out if existing ventilation controls (and other hazard control methods) are adequate.

Some workplaces may need a complete system of hoods and ducts to provide acceptable ventilation. Others may only require a single, well-placed exhaust fan. No special ventilation system may be needed for work with small amounts of organic peroxides which do not give off airborne contaminants.

Design and build ventilation systems for organic peroxides so that they do not result in an unintended hazard. Avoid organic materials, such as wood, unless the organic material is known to be non-reactive to the specific organic peroxides exhausted by the ventilation system. Use explosion-proof electrical equipment, and fans, shrouds and duct work made from materials compatible with the organic peroxides. Keep systems used for organic peroxides separate from systems exhausting incompatible substances.



Use non-combustible materials for air cleaning devices like dust collectors.

Locate exhaust openings near floor level, if necessary, to remove heavier-than-air vapours from storage areas.

Storage

Store organic peroxides according to the occupational health and safety regulations and fire and building codes that apply to your workplace. These laws may specify the kinds of storage areas, such as storage rooms and buildings, allowed for different formulations. They may also specify how to construct these storage areas, and the amounts of organic peroxides that can be stored in each area.

The following provides some general guidelines for storing organic peroxides safely.

Containers

Before storing, inspect all incoming containers to ensure that they are undamaged and properly labelled. Do not accept delivery of defective containers.

Store organic peroxides in the containers that the chemical supplier recommends. Normally, these are the same containers in which the material was shipped. Repackaging can be dangerous, especially when using contaminated or incompatible containers. For organic peroxides requiring temperature control, the recommended storage temperature range should be plainly marked on the container. Protect containers against impact or other damage. Do not use combustible pallets, such as wood, for storing organic peroxide containers.

Keep containers tightly closed to avoid contamination in storage. Storing open or partly open containers of peroxides diluted with solvents, including water, can lead to evaporation of the solvent. This can expose the more hazardous dry peroxide.

Some liquid organic peroxides, such as methyl ethyl ketone peroxide, gradually decompose giving off gas. These peroxides are shipped in containers with specially vented caps. Use no other type of cap for containers of these organic peroxides. The vent caps relieve the normal build-up of gas pressure that could shatter an unvented container. Check vent caps regularly to ensure that they are working properly. Keep vented containers in an upright position.

Storage Area

Store organic peroxides separately, away from processing and handling areas. Keep them away from incompatible materials such as strong acids and bases, other oxidizing materials, flammable or combustible liquids and materials that can be oxidized (often called reducing materials or



agents). Separate storage can reduce personal injury and damage caused in case of fires, spills or leaks.

Check the reactivity data and storage requirements sections of the MSDS for details about what materials are incompatible with a specific organic peroxide.

Construct walls, floors, shelving and fittings in storage areas from non-combustible materials that are compatible with the organic peroxides.

Ensure that floors are resistant to penetration by the organic peroxides in storage. Floors should have no cracks in which chemicals could lodge if spilled.

Since liquid organic peroxides flow easily, provide dikes around large liquid storage areas and sills or ramps at door openings. Store smaller amounts in trays made from compatible materials to contain spills or leaks.

Store containers at a convenient height for handling, below eye level if possible, to reduce the risk of dropping them.

Store organic peroxides in areas which are:

- well ventilated
- dry, cool, out of direct sunlight and away from steam pipes, boilers or other heat sources
- supplied with adequate firefighting equipment, including sprinklers
- supplied with suitable spill clean-up equipment and materials
- free of ignition sources such as open flames, hot surfaces, burning tools and spark-producing tools and devices
- accessible at all times
- labeled with suitable warning signs

Storage Temperatures

Follow the chemical supplier's recommendations for maximum and minimum temperatures for storage and use. Higher temperatures can be hazardous since they speed up the decomposition rate of organic peroxides. Where appropriate, keep the maximum storage temperature less than 38°C (100°F).

Some organic peroxides must be kept at low temperatures in refrigerators or freezers. Use only approved or specially modified units (generally known as "laboratory safe"). Standard domestic units contain many ignition sources inside the cabinet. If the storage area requires explosion-proof equipment, keep the refrigeration unit and all electrical equipment outside the area. Make connections between the refrigerator cabinet and the other equipment using tubing that passes through the wall of the storage area.

Locate refrigeration equipment in a well-ventilated area. This is needed to carry away peroxide decomposition products that might result from a refrigeration failure.



It can be hazardous to store organic peroxides below the minimum recommended temperatures. For example, acetyl peroxide, which is very shock-sensitive, is usually sold as a 25 percent solution in dimethyl phthalate to make it less sensitive. At temperatures below about -8°C (17°F), pure crystals of shock-sensitive acetyl peroxide form. Do not store organic peroxides which are diluted with water at temperatures below 0°C (32°F) to avoid separating out the pure organic peroxide.

Storage areas may need alarms that indicate when storage temperatures are higher or lower than required.

General Precautions

At all times:

- Allow only trained, authorized people into storage areas.
- Keep the amount of organic peroxides in storage as small as possible.
- Inspect storage areas regularly for any deficiencies including damaged or leaking containers and poor housekeeping.
- Correct all deficiencies as soon as possible.

Dispensing

Open and dispense containers of organic peroxides in a special room or area outside the storage area. Do not allow any ignition sources in the vicinity. Take care that the organic peroxides do not contact combustible or other incompatible materials when they are dispensed. Use containers and dispensing equipment such as drum pumps, scoops or spatulas that the chemical supplier recommends. These items must be made from non-sparking materials compatible with the peroxides used. Keep them very clean to avoid contamination.

Never transfer liquids by pressurizing their usual shipping containers with air or inert gas. The pressure may damage ordinary drums and barrels. Moreover, if air is used, it may create a flammable atmosphere inside the container.

Glass containers with screw-cap lids or glass stoppers may not be acceptable for some organic peroxides, especially those sensitive to friction and grinding. Never transfer materials stored in a vented container into a tightly sealed, non-vented container. The build-up of gas pressure could shatter it.

Dispense from only one container at a time. Finish all the dispensing of one material before starting to dispense another. Keep containers closed after dispensing to reduce the risk of contaminating their contents.

Never return unused material, even if it does not seem to be contaminated, to the original container.



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If a water-based formulation freezes, do not chip or grind it to break up lumps of material, or heat it to thaw it out. Follow the chemical supplier's advice.

In a safe place and at room temperature, slowly thaw organic peroxides that have crystallized out of solution. Do not heat the containers to speed up the process since an explosion might result.

Handling

Make sure that all areas where organic peroxides are used are clean and free of combustible and other incompatible materials and any ignition sources. Temperatures in peroxide use areas should not become high enough to cause rapid decomposition.

Processing Equipment

Processing equipment must be clean, properly designed and made from materials compatible with the organic peroxide being used. Find out from the chemical supplier what materials are suitable for the specific peroxide. Copper, brass or lead equipment is dangerous in contact with some organic peroxides at higher temperatures. Some steels and aluminum alloys, zinc and galvanized metal can also cause rapid decomposition of certain organic peroxides.

Diluting Organic Peroxides

Some jobs require diluting organic peroxides prior to use. Do this strictly according to the chemical supplier's advice. Using the wrong solvent or a contaminated solvent could cause an explosion. For example, methyl ethyl ketone peroxide and cyclohexanone peroxide may explode if they are mixed with acetone, a common solvent. Using reclaimed solvents of uncertain composition can also be hazardous. They may contain dangerous concentrations of contaminants that are incompatible with the organic peroxide.

Using Organic Peroxides with Resins

Organic peroxides are often used as catalysts to activate resins in plastics production. Never mix organic peroxides directly with any accelerators or promoters. A violent explosion may result. Thoroughly mix the accelerator or promoter in the resin mixture before adding the organic peroxide.

It is dangerous to dissolve peroxides in very small amounts of monomer (such as styrene) before adding them to the resin mixture. These "small quantity" mixtures can undergo rapid polymerization giving off a lot of heat. This may result in a fire.

General Precautions

Always:

- Inspect containers for damage or leaks before handling them.



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- Handle containers carefully to avoid damaging them.
- Make sure that containers are kept tightly closed except when actually using the material.
- Avoid returning used peroxides to containers of unused material.
- Keep only the smallest amounts possible (never more than one day's supply) of organic peroxides in the work area.
- Return unopened containers to the proper storage area and opened containers to a dispensing or premixing area at the end of the day.
- Check that all containers are properly labelled, and handle the containers so that the label remains undamaged and easy to read.

Disposal

Organic peroxide wastes are hazardous. Dispose of unwanted or contaminated organic peroxides promptly using a method the chemical supplier recommends. Consider organic peroxides accidentally mixed with an unknown or foreign material as contaminated. Never attempt to salvage spilled or contaminated organic peroxides.

Dispose of unused peroxide-resin mixes also. Allow partly cured wastes to set and cool in safe, open areas. Doing this helps to prevent the heat produced during the curing reaction from starting a fire in waste containers.

"Empty" drums, bottles, bags and other containers usually contain hazardous residues. Never use these containers for anything else, no matter how clean they seem. Treat them as organic peroxide wastes. Follow the chemical supplier's advice about how to safely handle or decontaminate "empty" containers.

Store organic peroxide waste in the same way as unused organic peroxides.

Never dispose of organic peroxides in ordinary garbage or down sinks or drains that connect to sanitary or storm sewers. Dispose of them according to the supplier's advice, or through hazardous waste collection and disposal companies. In all cases, dispose of organic peroxide wastes according to the environmental laws that apply to your jurisdiction. Contact the appropriate environmental officials for details.

Good Housekeeping

Maintain good housekeeping at all times in the workplace:

- Clean-up any spills promptly and safely according to directions in the MSDS.
- Be careful not to contaminate anything that can burn. A serious fire resulted when the same cotton rag was used to clean up both spilled organic peroxide and accelerator.

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- Do not use sawdust or other burnable sweeping compounds to clean up organic peroxide spills.
- Dispose of unlabelled or contaminated materials containing peroxides properly.
- Remove combustible wastes, including wood, paper and rags, promptly from work areas.
- Avoid any build-up of organic peroxide dusts on ledges or other surfaces.
- Ensure that all containers for waste are compatible with the organic peroxides used, properly marked and located close to the job.

Personal Cleanliness

Personal cleanliness helps protect you when you are working with organic peroxides:

- Wash hands before eating, drinking, smoking or going to the toilet.
- Remove contaminated clothing and footwear, since they can be a severe fire hazard.
- Wash contaminated items immediately and thoroughly in water before re-wearing or discarding.
- Do not wear or carry contaminated items into areas having ignition sources or where smoking is allowed.
- Store food and tobacco products in uncontaminated areas.
- Avoid touching yourself with contaminated hands.
- Wash thoroughly at the end of the workday.

Equipment Maintenance

Regular equipment maintenance can prevent leaks or emissions of organic peroxides into the workplace:

- Ensure that maintenance personnel know the possible hazards of the materials they may encounter and any special procedures and precautions needed before they begin work.
- Prevent leaks of grease or other lubricants from equipment where organic peroxides are used.
- Do not allow materials such as cleaning solvents, paints or thinners to contact organic peroxides.
- Be very careful when cutting, welding or doing other hot work on organic peroxide containers or equipment.



- Comply with applicable regulations and contact the chemical supplier for advice.

Personal Protective Equipment

If other methods, such as engineering controls, are not available or effective in controlling exposure to organic peroxides, wear suitable personal protective equipment (PPE). Choosing the right PPE for a particular job is essential. MSDSs should provide general guidance. Also obtain help from someone who knows how to evaluate the hazards of a specific job and how to select the proper PPE.

Avoid Skin Contact

Wear protective gloves, aprons, boots, hoods or other clothing, depending on the risk of skin contact. Choose clothing made of materials that resist penetration or damage by the chemical. The MSDS should recommend appropriate materials. If it does not, contact the chemical supplier for specific information.

Protect Your Eyes and Face

Always wear eye protection when working with organic peroxides. Avoid ordinary safety glasses. Use chemical safety goggles instead. In some cases, you should also wear a face shield to protect your face from splashes. The current Canadian Standards Association (CSA) Standard Z94.3, "Industrial Eye and Face Protectors," provides advice on selection and use of eye and face protectors.

Avoid Breathing Dust, Vapours or Mists

If respirators must be used for breathing protection, there should be a written respiratory protection program to follow. Guidance for developing a program can be found in the current CSA Standard Z94.4, "Selection, Care, and Use of Respirators." Follow all legal requirements for respirator use and approvals. These may vary between jurisdictions in Canada. Respirator cartridges or canisters containing oxidizable sorbents, such as activated charcoal, may not be acceptable if high airborne concentrations of organic peroxides are present. A hazardous reaction might occur.

Know and be familiar with the right PPE for emergencies, as well as normal operations.

Wear the PPE needed for doing a particular job. It cannot provide protection if it is not worn.

Handling Emergencies

Act fast in emergencies like chemical fires, spills and leaks.

- Evacuate the area at once if you are not trained to handle the problem or if it is clearly beyond your control.
- Alert other people in the area to the emergency.

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- Call the fire department immediately.
- Report the problem to the people responsible for handling emergencies where you work.
- Obtain first aid if you have been exposed to harmful chemicals and remove all contaminated clothes.

Check that emergency eyewash stations and safety showers are available wherever accidental exposure to organic peroxides that can damage skin or eyes might occur.

Only specially trained and properly equipped people should handle emergencies. Nobody else should go near the area until it is declared safe.

Planning, training and practising for emergencies help people to know what they must do.

The MSDSs for the materials used are a starting point for drawing up an emergency plan. MSDSs have specific sections on spill clean-up procedures, first aid instructions, and fire and explosion hazards including suitable fire extinguishing equipment and methods. If the directions in each MSDS section are unclear or seem incomplete, contact the material's supplier for help.

Many other sources can also help develop emergency plans. Local fire departments can assist with fire emergency plans and training. Occupational health and safety and environmental enforcement agencies, provincial safety associations, St. John Ambulance, insurance carriers, professional societies in occupational health and safety, labour unions, trade associations, some local colleges and universities and CCOHS can supply useful information at little or no cost. Specialized private consultants are also available.

5. BASIC SAFE PRACTICES

Following these basic safe practices will help protect you from the hazards of organic peroxides:

- Read the Material Safety Data Sheets (MSDSs) for all of the materials used in your work.
- Know all of the hazards (fire/explosion, health, corrosivity, chemical reactivity) of the materials used in your work.
- Know which of the materials you work with are organic peroxides.
- Store organic peroxides in suitable, labelled containers (usually their shipping containers) in a cool, dry area.
- Store, handle and use organic peroxides in well-ventilated areas and away from incompatible materials.



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- Follow the chemical supplier's advice about maximum and minimum storage and use temperatures.
- Eliminate ignition sources (sparks, smoking, flames, hot surfaces) when working with organic peroxides.
- Handle containers safely to avoid damaging them.
- Dispense organic peroxides carefully, using compatible equipment, into acceptable containers.
- Do not grind or subject organic peroxides to any type of friction or impact.
- Never return unused or contaminated organic peroxides to their original containers.
- Practice good housekeeping, personal cleanliness and equipment maintenance.
- Handle and dispose of organic peroxide wastes safely.
- Wear the proper personal protective equipment for each of the jobs you do.
- Know how to handle emergencies (fires, spills, personal injury) involving the organic peroxides you work with.
- Follow the health and safety rules that apply to your job.

Call the CCOHS Inquiries Service at 1-800-263-8466 if you need more information about how to work safely with organic peroxides.



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APPENDIX

**Some Typical Organic Peroxide Formulations Classified
According to Their Fire and Explosion Hazard***

Class	Peroxide	Concentration, Weight Percent	Diluted with	Maximum Individual Container Size
Class I	Acetyl cyclohexane sulfonyl peroxide	60-65	Water	1 lb R
	Benzoyl peroxide	98+	--	1 lb
	t-Butyl hydroperoxide	90	t-BuOH	5 gal
	t-Butyl peroxyacetate	75	OMS	5 gal
	Di-n-propyl peroxydicarbonate	98	--	1 gal R
		85	OMS	1 gal R

Class II	Acetyl peroxide	25	DMP	5 gal
	t-Butyl hydroperoxide	70	DTBP and t-BuOH	55 gal
	t-Butyl peroxy-2-ethyl-hexanoate	97	--	55 gal R
	Peroxyacetic acid	43	Water, acetic acid and hydrogen peroxide	30 gal

Class III	Benzoyl peroxide	78	Water	25 lb
	Benzoyl peroxide paste	50-55	BBP	380 lb
	Cumene hydroperoxide	86	Cumene	55 gal
	Decanoyl peroxide	98.5	--	100 lb R
	Di-t-Butyl peroxide	99	--	55 gal
	Diisopropyl peroxydicarbonate	30	Toluene	5 gal R
	Methyl ethyl ketone (MEK) peroxide	9% active oxygen	DMP	5 gal

* Adapted from National Fire Protection Association (NFPA) 43B--Code for the Storage of Organic Peroxide Formulations, 1986 edition.



APPENDIX, continued

Class	Peroxide	Concentration, Weight Percent	Diluted with	Maximum Individual Container Size
Class IV	Benzoyl peroxide	70	Water	25 lb
	Benzoyl peroxide paste	50	BBP and water	380 lb
	Benzoyl peroxide slurry	40	Water and plasticizer	380 lb
	Benzoyl peroxide powder	35	Starch	100 lb
	t-Butyl hydroperoxide	70	Water	55 gal
	Lauroyl peroxide	98	--	110 lb
	MEK peroxide	5.5% active oxygen	DMP	5 gal
	MEK peroxide	9% active oxygen	Water and glycols	5 gal

Class V	Benzoyl peroxide	35	Dicalcium phosphate dihydrate or calcium sulphate	100 lb
	1,1-Di-t-butyl peroxy- 3,5,5-trimethyl cyclohexane	40	Calcium carbonate	100 lb
	2,5-Dimethyl-2,5-di- (5-butylperoxy) hexane	47	Inert solid	100 lb
	2,4-Pentanedione peroxide	4% active oxygen	Water and solvent	5 gal

R - Refrigeration required
t-BuOH - tertiary Butanol
OMS - Odourless mineral spirits
DMP - Dimethyl phthalate

DTBP - Ditertiary butyl phthalate
BBP - Butyl benzyl phthalate
gal - 1 U.S. gallon = 3.785 litres



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